

## Supplementary Information

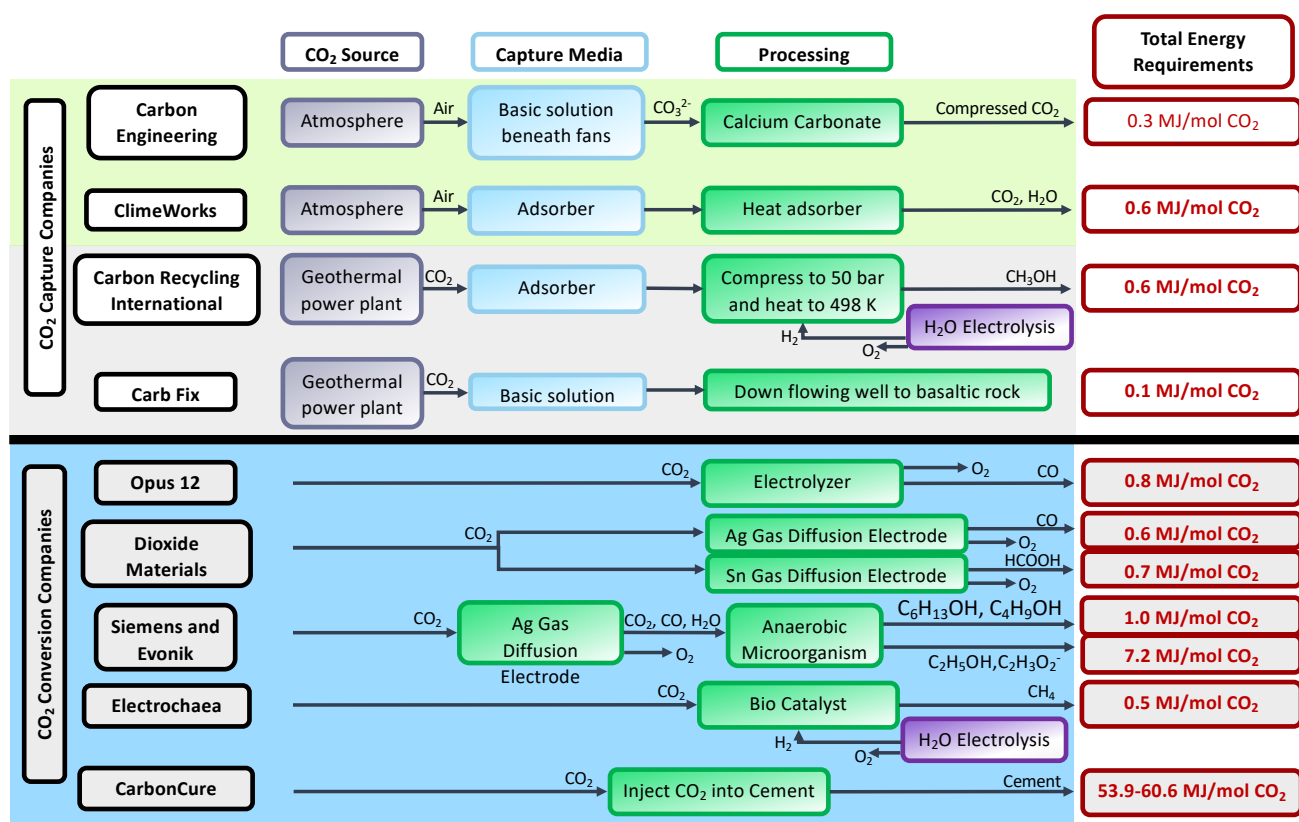
### **Bicarbonate or Carbonate Processes for Coupling Carbon Dioxide Capture and Electrochemical Conversion**

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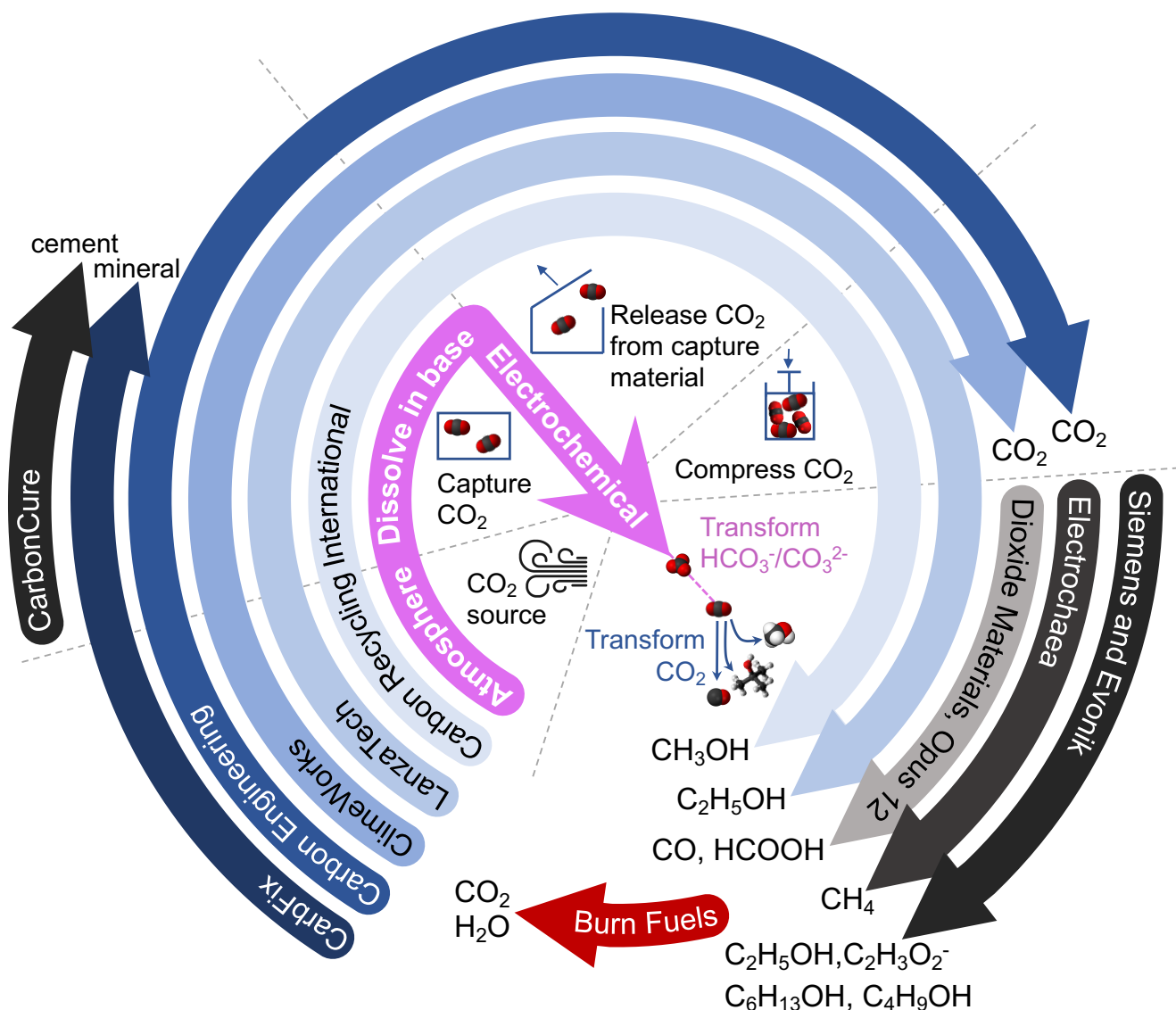
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Supplementary Figure 1: Schematic representation of various pilot plants that capture CO<sub>2</sub> and/or transform it to either concentrated and pressurized CO<sub>2</sub> or to a value-added product. The companies in the light blue region capture CO<sub>2</sub> from the atmosphere. The companies in the mid-blue region capture CO<sub>2</sub> from concentrated sources. The companies in the dark blue region focus only on transforming already captured CO<sub>2</sub>. The energies reported for these companies does not include the energy required to capture the CO<sub>2</sub>. The energy reported for the electrolyzer systems assume 100% conversion efficiency of CO<sub>2</sub> which is not realistic, so there would be additional energy costs for a recirculating system.



Supplementary Figure 2: Schematic representation of the steps for various prototype systems designed to capture CO<sub>2</sub> and/or convert it to either concentrated and pressurized CO<sub>2</sub> or to a value-added product. The blue arrows represent prototype processes that capture and convert CO<sub>2</sub>, grey arrows represent prototype processes that only focus on CO<sub>2</sub> conversion, and the pink arrow represents the process that we propose.

## **Section I: Energy Input Calculations for CO<sub>2</sub> Capture and Conversion Processes**

### **A: Carbon Engineering**

Carbon Engineering uses fans to contact air with a basic solution, thus dissolving CO<sub>2</sub> and transforming it into carbonate.<sup>1</sup> The carbonate reacts with Ca(OH)<sub>2</sub> to form CaCO<sub>3</sub>, which is then heated to release pure CO<sub>2</sub> for compression and storage. Carbon Engineering reports that their process for capturing CO<sub>2</sub> from the air requires 8.81 GJ per 1.3-1.5 metric tons of pure and compressed CO<sub>2</sub> produced. Below we convert this value to kJ/mol CO<sub>2</sub> so that the value can be readily compared to other processes reported.

$$\begin{aligned} \text{Energy} &= \frac{8.81 \text{ GJ}}{1.3 - 1.5 \text{ t pure CO}_2} \times \frac{1 \text{ t pure CO}_2}{1000 \text{ kg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{44.01 \text{ g}}{1 \text{ mol CO}_2} \times \frac{1000000 \text{ kJ}}{1 \text{ GJ}} \\ &= \frac{259 \text{ to } 298 \text{ kJ}}{\text{mol CO}_2} \end{aligned}$$

We would like to note that Carbon Engineering has now reported that they have also developed a process to make liquid fuels with their captured CO<sub>2</sub>. They estimate the cost will be \$1/L once the process is scaled up.<sup>2</sup> However, they do not report any details on how they do this, what specific fuel they synthesize, or the energy requirements of the process, so we will not discuss this process further.

### **B: CarbFix**

Ragnheidardottir, E., et al.<sup>3</sup> reports that the power requirement for the CarbFix pilot plant is 200 kW and it stores 2099 metric tons of CO<sub>2</sub> annually. Below we use these values to convert to kJ/mol CO<sub>2</sub> so that the value can be readily compared to other processes reported.

$$\begin{aligned} \text{Energy} &= \frac{200 \text{ kJ}}{\text{s}} \times \frac{3600 \text{ sec}}{1 \text{ hr}} \times \frac{24 \text{ hrs}}{1 \text{ day}} \times \frac{365 \text{ days}}{1 \text{ yr}} \times \frac{1 \text{ yr}}{2099 \text{ t CO}_2} \times \frac{1 \text{ t CO}_2}{1000 \text{ kg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \\ &\quad \times \frac{44.01 \text{ g}}{1 \text{ mol CO}_2} = \frac{132 \text{ kJ}}{\text{mol CO}_2} \end{aligned}$$

### **C: Carbon Recycling International**

Kauw, M. et al.<sup>4</sup> report that the Carbon Recycling International 5M plant consumes 47.9 MJ/kg methanol. Below we convert this value to kJ/mol CO<sub>2</sub> so that the value can be readily compared to other processes reported.

$$\begin{aligned} \text{Energy} &= \frac{47.9 \text{ MJ}}{\text{kg methanol}} \times \frac{1000 \text{ kJ}}{1 \text{ MJ}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{32.04 \text{ g}}{1 \text{ mole methanol}} \times \frac{1 \text{ mol methanol}}{1 \text{ mole CO}_2} \\ &= \frac{1535 \text{ kJ}}{\text{mol CO}_2} \end{aligned}$$

### **D: Opus12**

Opus 12 reports that their pilot device uses 5kW and produces 15kg of CO per day, and the input is concentrated CO<sub>2</sub>.<sup>5</sup> We assume for these devices that the conversion percentage of CO<sub>2</sub> is 100%. Below we convert these values to kJ/mol CO<sub>2</sub> so that the value can be readily compared to other processes reported.

$$Energy = \frac{1 \text{ day}}{15000g \text{ CO}} \times \frac{24 \text{ hrs}}{1 \text{ day}} \times \frac{3600 \text{ sec}}{1 \text{ hr}} \times \frac{5 \text{ kJ}}{1 \text{ sec}} \times \frac{28.01 \text{ g}}{1 \text{ mol CO}} \times \frac{1 \text{ mol CO}}{1 \text{ mole CO}_2} = \frac{807 \text{ kJ}}{\text{mol CO}_2}$$

### E: Dioxide Materials

Dioxide Materials provides information on the voltage at which to run their devices, the Faradaic efficiency, and the stability of the devices.<sup>6,7</sup> The electrolyzer that takes CO<sub>2</sub> to CO runs at 500mA/cm<sup>2</sup> at 3V full cell potential with a FE of 95%. The cathode is made of a Ag catalyst and the membrane is made of Sustanion, leading to a device stability of over 3000 hours.<sup>7</sup> The electrolyzer that takes CO<sub>2</sub> to formic acid runs at 160mA/cm<sup>2</sup> at 3.5V full cell potential with a FE of 90%. The cathode is made of an Sn nanoparticle catalyst, the membrane is made of Sustanion, and the counter is IrO<sub>2</sub>.<sup>6</sup> We assume for these devices that the conversion percentage of CO<sub>2</sub> is 100%. We take this information and calculate the energy in kJ/mol CO<sub>2</sub>.

For CO<sub>2</sub> to CO electrolyzer

$$Energy = \frac{UzF}{FE} = \frac{(3 \text{ V})(2 \text{ mole electrons})(96485 \text{ C mol}^{-1})}{.95} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \frac{609 \text{ kJ}}{\text{mol CO}_2}$$

For CO<sub>2</sub> to Formic Acid electrolyzer

$$Energy = \frac{UzF}{FE} = \frac{(3.5 \text{ V})(2 \text{ mole electrons})(96485 \text{ C mol}^{-1})}{.90} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \frac{750 \text{ kJ}}{\text{mol CO}_2}$$

### F: Cement production

World Coal Association reports that it requires 200kg of coal to produce 1 metric ton of cement.<sup>8</sup> The higher heating value of coal is approximately 28.8-32.4 MJ/kg of coal according to the European Nuclear Society.<sup>9</sup> Carbon Cure can store 25 lbs of CO<sub>2</sub> per cubic yard of cement.<sup>10</sup> From these values we were able to calculate the amount of energy required per mol of CO<sub>2</sub> stored in the cement.

$$Energy \cong \frac{200 \text{ kg coal}}{1 \text{ tonne cement}} \times \frac{28.8 \text{ to } 32.4 \text{ MJ}}{1 \text{ kg coal}} \times \frac{1000 \text{ kJ}}{1 \text{ MJ}} \times \frac{1 \text{ tonne}}{1000 \text{ kg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{3.15 \text{ g cement}}{1 \text{ cm}^3} \\ \times \frac{764555 \text{ cm}^3}{1 \text{ yd}^3} \times \frac{1 \text{ yd}^3}{25 \text{ lb CO}_2} \times \frac{1 \text{ lb}}{453.6 \text{ g}} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} = \frac{53,837 \text{ to } 60,567 \text{ kJ}}{\text{mol CO}_2}$$

### G: Siemens and Evonik

Haas, T., et al.<sup>11</sup> report a system designed in collaboration between Siemens and Evonik.<sup>11</sup> This system uses a CO<sub>2</sub> electrolyzer to make syngas which is then fermented in the presence of bacteria. Depending on the type of bacteria, operating conditions, and ratio of CO to H<sub>2</sub>, the fermenters either produce a 1:1 mixture of hexanol and butanol or a combination of acetate and ethanol. For the hexanol and butanol they report that this process requires 22kWh/kg of alcohol and then an additional 0.6 kWh/kg hexanol to

separate the alcohols. For the acetate and ethanol process they apply 4.94V over the whole CO<sub>2</sub> electrolyzer. The fermenter is put at 36°C.<sup>11</sup> We assume that the fermenter has a specific heat capacity of water to calculate the energy required to heat it. We then add the energy for the electrolyzer to the energy of the fermenter to obtain a final energy, this energy does not include the energy required to separate the products. In a practical system there would also be energy costs for pumps, feeding the bacteria, capturing the CO<sub>2</sub>, etc. which we have not taken into account here.

For CO<sub>2</sub> to hexanol and butanol

$$Energy = \frac{22.6 \text{ kWh}}{\text{kg alcohol}} \times \frac{3600 \text{ sec}}{1 \text{ hr}} \times \frac{1 \text{ kg alcohol}}{1000 \text{ g}} \times \frac{.5 (74.12 + 102.17) \text{ g}}{1 \text{ mol alcohol}} = \frac{7,171 \text{ kJ}}{\text{mol alcohol}}$$

For CO<sub>2</sub> to acetate and ethanol

$$Energy = \frac{UzF}{FE} = \frac{(4.94 \text{ V})(2 \text{ mole electrons})(96485 \text{ C mol}^{-1})}{1} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \frac{953 \text{ kJ}}{\text{mol}}$$

$$Q_{\text{water}} = mc\Delta T = \left(2 \text{ L H}_2\text{O} \times \frac{1 \text{ mole}}{22.4 \text{ L}}\right) \times \frac{18.02 \text{ g}}{1 \text{ mole H}_2\text{O}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \left(\frac{4.181 \text{ kJ}}{\text{kg K}}\right) (309 - 293 \text{ K})$$

$$= \frac{0.11 \text{ kJ}}{\text{mol H}_2\text{O}}$$

## **H: Electrochaeta<sup>12</sup>**

For a BioCat 10 reaction the reported installed power is 220kW, the input of CO<sub>2</sub> is 500 Nm<sup>3</sup>/h, the input of H<sub>2</sub> is 2000 Nm<sup>3</sup>/h. The output is 500 Nm<sup>3</sup>/h CH<sub>4</sub>.<sup>12</sup>

$$Energy = \frac{220 \text{ kJ}}{1 \text{ s}} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ h}}{500 \text{ Nm}^3 \text{ CO}_2} \times \frac{1 \text{ Nm}^3}{1000 \text{ L}} \times \frac{22.4 \text{ L}}{1 \text{ mol CO}_2} = \frac{36 \text{ kJ}}{\text{mol CO}_2}$$

We assume use of an NEL H<sub>2</sub>O electrolyzer to produce the H<sub>2</sub>.<sup>4</sup>

$$Energy = \frac{52 \text{ kWh}}{1 \text{ kg H}_2} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{.002 \text{ kg H}_2}{1 \text{ mol H}_2} = \frac{374 \text{ kJ}}{\text{mol H}_2}$$

## **Section 2: Energy Input Calculations for Bicarbonate or Carbonate Feedstock Systems**

### **A: Energy required to dissolve CO<sub>2</sub> in solutions of various alkalinity**

Keith, D., et al.<sup>13</sup> report an air contactor that requires 61 kWh/tCO<sub>2</sub> for the fan which is 70% efficient and 21 kWh/tCO<sub>2</sub> for the fan which is 82% efficient.<sup>13</sup> In the air contactor described in this paper they have a basic solution comprised of 2M K<sup>+</sup>, 0.45M CO<sub>3</sub><sup>2-</sup>, 1.1M OH<sup>-</sup>.<sup>13</sup> We have calculated the energy in kJ/mol CO<sub>2</sub> assuming this solution concentration and for a solution comprised of 2.24M K<sup>+</sup>, 2.24M HCO<sub>3</sub><sup>-</sup>, 10<sup>-4.78</sup>M OH<sup>-</sup>.

Energy to dissolve CO<sub>2</sub> in solution to make carbonate

Solution: 2M K<sup>+</sup>, 0.45M CO<sub>3</sub><sup>2-</sup>, 1.1M OH<sup>-</sup>

$$\frac{61 \text{ kWh} + 21 \text{ kWh}}{1 \text{ tCO}_2} \times \frac{3600 \text{ sec}}{1 \text{ hr}} \times \frac{1 \text{ tCO}_2}{1000 \text{ kg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol}} = \frac{13 \text{ kJ}}{\text{mol CO}_2}$$

Energy to dissolve CO<sub>2</sub> in solution to make bicarbonate

Solution: 2.24M K<sup>+</sup>, 2.24M HCO<sub>3</sub><sup>-</sup>, 10<sup>-4.78</sup>M OH<sup>-</sup>

$$\frac{61 \text{ kWh}}{1 \text{ t CO}_2} + \frac{21 \text{ kWh}}{1 \text{ t CO}_2} \times \frac{0.45 \text{ M CO}_3^{2-}}{2.24 \text{ M HCO}_3^-} = \frac{65 \text{ kJ}}{\text{mol CO}_2}$$

$$\frac{65 \text{ kWh}}{1 \text{ t CO}_2} \times \frac{3600 \text{ sec}}{1 \text{ hr}} \times \frac{1 \text{ t CO}_2}{1000 \text{ kg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol}} = \frac{10 \text{ kJ}}{\text{mol CO}_2}$$

#### **B: Bipolar membrane with Ag catalyst cathode and Ni foam anode**

Sargent, E., et al.<sup>14</sup> reports a carbonate electrolyzer that uses a Ag catalyst cathode and a Ni foam anode separated by a bipolar membrane. The catholyte is a carbonate solution and the anolyte is a potassium hydroxide solution. The device is tested at various potentials; for our calculations we choose to look at when the applied a full cell potential of 3.8V, which gives the appropriate ratio of CO to H<sub>2</sub>.<sup>14</sup>

$$\text{Energy} = \frac{UzF}{FE} = \frac{(3.8V)(2 \text{ mole electrons})(96485.33212 \text{ C mol}^{-1})}{1} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \frac{733 \text{ kJ}}{\text{mol CO}_2}$$

This energy does not take into account the energy of the pumps or other practical considerations that would be needed for a functional system.

#### **C: Bipolar membrane with Ag catalyst cathode and Ni anode**

Li, T., et al.<sup>15</sup> reports an electrolyzer that uses a Ag catalyst at the cathode and a Ni anode to transform a solution of bicarbonate into syngas. When 3.5V is applied over the full cell the appropriate ratio of H<sub>2</sub> and CO are produced. Below we calculate the energy this corresponds to.<sup>15</sup>

$$\text{Energy} = \frac{UzF}{FE} = \frac{(3.5 \text{ V})(2 \text{ mole electrons})(96485 \text{ C mol}^{-1})}{1} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \frac{675 \text{ kJ}}{\text{mol CO}_2}$$

This energy does not take into account the energy of the pumps or other practical considerations that would be needed for a functional system.

#### **D: Area required of electrolyzer, capture system, and solar cells**

We calculate the area required for a plant able to process 1 metric ton of CO<sub>2</sub> per day (t-CO<sub>2</sub>/day) and how much area would be needed to convert the 37.1 gigatons of CO<sub>2</sub> emitted globally annually.<sup>16</sup> We also assume that the plant is operates continuously for 24 hours, all power needs are generated on site via solar energy, and that there is sufficient battery storage to power the capture and conversion

system continuously. We assume that the capture system is designed in the same way as Carbon Engineering's air contactor. They report that their air contactor processes 22 t-CO<sub>2</sub>/m<sup>2</sup>/yr and that the plant they describe in their report can capture 1 t-CO<sub>2</sub>/day.<sup>13</sup> For the electrolyzer we assume that the metrics from the electrolyzer reported by Sargent, et al. – 200 mA/cm<sup>2</sup> at 3.8 V.<sup>17</sup> For the solar system we assume a 350 W solar panels with an area of 2.03 m<sup>2</sup>.<sup>18</sup> The average capacity factor in the united states is approximately 25%.<sup>19</sup>

Calculate area of capture system to capture 1 t-CO<sub>2</sub> per day

$$Total\ Area = \frac{1\ t - CO_2}{day} \times \frac{365\ day}{1\ year} \times \frac{m^2 * year}{22\ t - CO_2} = 16.6\ m^2$$

Calculate area of electrolyzer to convert 1 t-CO<sub>2</sub> per day

$$\begin{aligned} Total\ Area &= \frac{0.2\ C}{cm^2 * sec} \times \frac{10000\ cm^2}{1\ m^2} \times \frac{1\ mol\ CO_2}{3\ mol\ syngas} \times \frac{60\ sec}{1\ min} \times \frac{60\ min}{1\ hr} \times \frac{24\ hr}{1\ day} \\ &\times \frac{1\ electron}{1.6 * 10^{-19}\ C} \times \frac{1\ CO_2\ molecule\ converted}{2\ electron} \times \frac{6.022 * 10^{23}\ CO_2\ molecule}{1\ mole\ CO_2} \\ &\times \frac{.04401\ kg}{1\ mol\ CO_2} \times \frac{1\ ton}{1000\ kg} = \frac{2.36\ ton\ CO_2}{m^2 * day} = \frac{1\ ton\ CO_2}{0.38\ m^2 * day} \end{aligned}$$

Calculate area of photovoltaic system needed to power plant that processes 1 t-CO<sub>2</sub> per day

$$\begin{aligned} Power\ density &= \frac{350\ W}{2.03\ m^2} \times 0.25 \times 24\ hr = \frac{1.03\ kWh}{1\ m^2} \\ Total\ Area &= \frac{746\ kJ}{mol\ CO_2} \times \frac{1\ mol\ CO_2}{.04401\ kg} \times \frac{1000\ kg}{1\ ton} \times \frac{0.0002778\ kWh}{1\ kJ} \times \frac{1\ m^2}{1.03\ \frac{kWh}{day}\ solar\ panel} \\ &= \frac{4571\ m^2}{tCO_2/day} \sim \frac{0.005\ km^2}{tCO_2/day} \end{aligned}$$

Calculate area of whole system needed to process CO<sub>2</sub> emitted globally daily

$$\begin{aligned} Total\ area &= \frac{37.1 * 10^9\ tons\ CO_2}{1\ yr} \times \frac{1\ yr}{365\ days} \times \frac{4571\ m^2}{tCO_2/day} \times \frac{1\ km^2}{(1000\ m)^2} \\ &= 464,614\ km^2 \sim 460,000\ km^2 \end{aligned}$$

### **E: Energy required to make syngas from coal**

Energy Technology Systems Analysis Programme reports that the process of synthesizing syngas from coal is roughly 74.7% efficient.<sup>20</sup> Syngas has roughly half of the energy density of natural gas. From this we can estimate the energy required to make syngas.



$$E = 0.5 \times \frac{33.4 - 82.7 \text{ MJ}}{1 \text{ m}^3 \text{ natural gas}} \times \frac{1 \text{ m}^3}{1000 \text{ L}} \times \frac{22.4 \text{ L}}{1 \text{ mol syngas}} \times \frac{3 \text{ mol syngas}}{1 \text{ mol CO}} \times \frac{100}{74.7} = \frac{1.5 - 3.7 \text{ MJ}}{\text{mol CO}}$$

#### **F: Energy required to make syngas from natural gas using steam reforming and the reverse water gas shift with CO<sub>2</sub> capture**

For the process of steam reforming natural gas and then performing the reverse water gas shift to obtain the proper ratio of CO to H<sub>2</sub> there are many steps involved. Baltrusaitis, J. and W. Luyben<sup>21</sup> report that the energy for the preheater is 10.47 MW, vaporizer is 202.9 MW, steam methane reforming is 536.6 MW, the furnace for the reverse water gas shift is 121.2 MW, heat exchanger two is 219.8 MW, heat exchanger is 46 MW, the steam methane reforming cooler is 177.2 MW, the reboiler is 75.2 MW, the feed effluent heat exchanger is 53.2 MW, the condenser is 30.2 MW, the compressor is 9.83 MW, the intercoolers are 10.76 MW, and the stripper cooler is 40.86 MW. There are also some additional smaller energies that total 400MW. This system produces 15,013 kmol/h H<sub>2</sub>, 7500 kmol/h CO, 271 kmol/h CH<sub>4</sub>, and 94 kmol/h H<sub>2</sub>O. From this we can calculate the energy needed to make the syngas.

$$\begin{aligned} \text{Total power} &= 10.47 \text{ MW} + 202.9 \text{ MW} + 536.6 \text{ MW} + 121.2 \text{ MW} + 46 \text{ MW} + 177.2 \text{ MW} + 75.2 \text{ MW} \\ &\quad + 53.2 \text{ MW} + 30.2 \text{ MW} + 9.83 \text{ MW} + 10.76 \text{ MW} + 40.86 \text{ MW} + 400 \text{ MW} \\ &= 1,314.4 \text{ MW} \end{aligned}$$

$$E = \frac{1314.4 \text{ MJ}}{1 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{1 \text{ hr}}{7500 \text{ kmol CO}} \times \frac{1 \text{ kmol}}{1000 \text{ mol}} = \frac{0.8 \text{ MJ}}{\text{mol CO}}$$

#### **G: Energy required to make syngas from natural gas using steam reforming and the reverse water gas shift**

For the process of steam reforming natural gas and then performing the reverse water gas shift to obtain the proper ratio of CO to H<sub>2</sub> there are many steps involved. Baltrusaitis, J. and W. Luyben<sup>21</sup> report that the energy for the preheater is 10.47 MW, vaporizer is 202.9 MW, steam methane reforming is 536.6 MW, the furnace for the reverse water gas shift is 121.2 MW, heat exchanger two is 219.8 MW, heat exchanger 3 is 46 MW, compressor is 9.83MW, and the steam methane reforming cooler is 177.2 MW here are also some additional smaller energies that total 400MW. This system produces 15,013 kmol/h H<sub>2</sub>, 7500 kmol/h CO, 272 kmol/h CH<sub>4</sub>, and 75 kmol/h H<sub>2</sub>O. From this we can calculate the energy needed to make the syngas.

$$\begin{aligned} \text{Total power} &= 10.47 \text{ MW} + 202.9 \text{ MW} + 536.6 \text{ MW} + 121.2 \text{ MW} + 46 \text{ MW} + 177.2 \text{ MW} \\ &\quad + 9.83 \text{ MW} + 400 \text{ MW} = 1,504.2 \text{ MW} \end{aligned}$$

$$E = \frac{1314.4 \text{ MJ}}{1 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{1 \text{ hr}}{7500 \text{ kmol CO}} \times \frac{1 \text{ kmol}}{1000 \text{ mol}} = \frac{0.7 \text{ MJ}}{\text{mol CO}}$$

#### **H: Pd-Pt cathode with Pt anode to reduce bicarbonate to formate**

Kortlever, R., et al. reports an electrochemical cell that reduces bicarbonate to formate at low overpotentials using a Pd-Pt cathode and Pt anode. A potential of -0.4V vs the reversible hydrogen electrode (RHE) is applied to the cathode, which corresponds to ~90% faradaic efficiency for formate.<sup>22</sup> We assume a full cell potential of 2V, since the cell has some resistance and the anode is performing OER which has a standard potential of 1.23V. We have calculated the energy used by the cell below,

the calculation does not include the energy that would be required for pumps or other practical considerations.

$$Energy = \frac{UzF}{FE} = \frac{(2 V)(2 \text{ mole electrons})(96485 \text{ C mol}^{-1})}{.90} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \frac{429 \text{ kJ}}{\text{mol CO}_2}$$

#### **H: Production of Sodium Hydroxide**

The Office of Energy Efficiency and Renewable Energy of the U.S. Department of Energy report that when a zero-gap membrane chlor-alkali cell with an oxygen-depolarized cathode is used for the chlor-alkali process, sodium hydroxide can be produced for 2,500 kWh/ton.<sup>23</sup>

$$Energy = \frac{2,500 \text{ kWh}}{1 \text{ ton NaOH}} * \frac{3600 \text{ kJ}}{1 \text{ kWh}} \times \frac{1 \text{ ton}}{1000 \text{ kg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{39.997 \text{ g NaPH}}{1 \text{ mol NaOH}} = \frac{360 \text{ kJ}}{\text{mol NaOH}}$$

### **Section 3: CO<sub>2</sub> Electrolyzer Conversion Efficiencies**

For all calculations in this section we assume that the CO<sub>2</sub> is at standard temperature and pressure.

#### **A: Gewirth, A., et al CO<sub>2</sub> to electrolyzer<sup>24</sup>**

$$\text{Mols of CO}_2 \text{ per second} = \left( \frac{7 \text{ ml CO}_2}{1 \text{ min}} \right) \left( \frac{1 \text{ min}}{60 \text{ s}} \right) \left( \frac{22,400 \text{ ml CO}_2}{1 \text{ mol CO}_2} \right) = \frac{5.2 * 10^{-6} \text{ mol CO}_2}{1 \text{ s}}$$

$$\text{Mols of ethylene per second} = \left( \frac{.17 \text{ C}}{1 \text{ s}} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol ethylene}}{12 \text{ mol e}^-} \right) = \frac{1.5 * 10^{-10} \text{ mol CO}}{1 \text{ s}}$$

$$\text{Mols of ethanol per second} = \left( \frac{.09 \text{ C}}{1 \text{ s}} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol ethanol}}{12 \text{ mol e}^-} \right) = \frac{7.8 * 10^{-11} \text{ mol CO}}{1 \text{ s}}$$

$$\text{Conversion Percentage} = \frac{2.2 * 10^{-10} \text{ mol C}_2}{1 \text{ s}} * \frac{1 \text{ s}}{5.2 * 10^{-6} \text{ mol CO}_2} = 0.004\%$$

#### **B: Siemens and Evonik CO<sub>2</sub> electrolyzer<sup>11</sup>**

$$\text{Mols of CO}_2 \text{ per second} = \left( \frac{90 \text{ ml CO}_2}{1 \text{ min}} \right) \left( \frac{1 \text{ min}}{60 \text{ s}} \right) \left( \frac{22,400 \text{ ml CO}_2}{1 \text{ mol CO}_2} \right) = \frac{6.7 * 10^{-5} \text{ mol CO}_2}{1 \text{ s}}$$

$$\text{Mols of Formate per second} = \left( \frac{.3 \text{ C}}{1 \text{ s}} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol CO}}{2 \text{ mol e}^-} \right) * .7 = \frac{1.1 * 10^{-6} \text{ mol CO}}{1 \text{ s}}$$

$$\text{Conversion Percentage} = \frac{1.1 * 10^{-6} \text{ mol CO}}{1 \text{ s}} * \frac{1 \text{ s}}{6.7 * 10^{-5} \text{ mol CO}_2} = 1.6\%$$

**C: Sargent, E., et al CO<sub>2</sub> electrolyzer<sup>25</sup>**

$$\text{Mols of CO}_2 \text{ per second} = \left( \frac{30 \text{ ml CO}_2}{1 \text{ min}} \right) \left( \frac{1 \text{ min}}{60 \text{ s}} \right) \left( \frac{22,400 \text{ ml CO}_2}{1 \text{ mol CO}_2} \right) = \frac{2.2 * 10^{-5} \text{ mol CO}_2}{1 \text{ s}}$$

$$\begin{aligned} \text{Mols of Acetic acid per second} &= \left( \frac{.75 \text{ C}}{1 \text{ s}} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol acetic acid}}{8 \text{ mol e}^-} \right) * .05 \\ &= \frac{4.8 * 10^{-8} \text{ mol acetic acid}}{1 \text{ s}} \end{aligned}$$

$$\begin{aligned} \text{Mols of ethylene per second} &= \left( \frac{.75 \text{ C}}{1 \text{ s}} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol ethylene}}{12 \text{ mol e}^-} \right) * .65 \\ &= \frac{4.2 * 10^{-7} \text{ mol CO}}{1 \text{ s}} \end{aligned}$$

$$\text{Mols of ethanol per second} = \left( \frac{.75 \text{ C}}{1 \text{ s}} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol ethanol}}{12 \text{ mol e}^-} \right) * .1 = \frac{6.4 * 10^{-8} \text{ mol CO}}{1 \text{ s}}$$

$$\text{Conversion Percentage} = \frac{5.3 * 10^{-7} \text{ mol C}_2}{1 \text{ s}} * \frac{1 \text{ s}}{2.2 * 10^{-5} \text{ mol CO}_2} = 2.4\%$$

**D: Kenis, P., et al CO<sub>2</sub> electrolyzer<sup>26</sup>**

$$\text{Mols of CO}_2 \text{ per second} = \left( \frac{7 \text{ ml CO}_2}{1 \text{ min}} \right) \left( \frac{1 \text{ min}}{60 \text{ s}} \right) \left( \frac{22,400 \text{ ml CO}_2}{1 \text{ mol CO}_2} \right) = \frac{5.2 * 10^{-6} \text{ mol CO}_2}{1 \text{ s}}$$

$$\text{Mols of CO per second} = \left( \frac{.275 \text{ C}}{1 \text{ s}} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol CO}}{2 \text{ mol e}^-} \right) * = \frac{1.4 * 10^{-6} \text{ mol CO}}{1 \text{ s}}$$

$$\text{Conversion Percentage} = \frac{5.3 * 10^{-7} \text{ mol CO}}{1 \text{ s}} * \frac{1 \text{ s}}{2.2 * 10^{-5} \text{ mol CO}_2} = 27.3\%$$

**E: Kenis, P., et al CO<sub>2</sub> electrolyzer<sup>27</sup>**

$$\text{Mols of CO}_2 \text{ per second} = \left( \frac{7 \text{ ml CO}_2}{1 \text{ min}} \right) \left( \frac{1 \text{ min}}{60 \text{ s}} \right) \left( \frac{22,400 \text{ ml CO}_2}{1 \text{ mol CO}_2} \right) = \frac{5.2 * 10^{-6} \text{ mol CO}_2}{1 \text{ s}}$$

$$\text{Mols of CO per second} = \left( \frac{.375 \text{ C}}{1 \text{ s}} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol CO}}{2 \text{ mol e}^-} \right) = \frac{1.8 * 10^{-6} \text{ mol CO}}{1 \text{ s}}$$

$$\text{Conversion Percentage} = \frac{5.3 * 10^{-7} \text{ mol CO}}{1s} * \frac{1s}{2.2 * 10^{-5} \text{ mol CO}_2} = 34.8\%$$

**F: Xuan, J., et al CO<sub>2</sub> electrolyzer<sup>28</sup>**

$$\text{Mols of CO}_2 \text{ per second} = \left( \frac{50 \text{ ml CO}_2}{1 \text{ min}} \right) \left( \frac{1 \text{ min}}{60s} \right) \left( \frac{22,400 \text{ ml CO}_2}{1 \text{ mol CO}_2} \right) = \frac{3.7 * 10^{-5} \text{ mol CO}_2}{1s}$$

$$\text{Mols of formate per second} = \left( \frac{.350 \text{ C}}{1s} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol HCOO}^-}{2 \text{ mol e}^-} \right) = \frac{1.8 * 10^{-6} \text{ mol HCOO}^-}{1s}$$

$$\text{Conversion Percentage} = \frac{1.8 * 10^{-6} \text{ mol HCOO}^-}{1s} * \frac{1s}{3.7 * 10^{-5} \text{ mol CO}_2} = 4.9\%$$

**G: Lv, J. J., et al CO<sub>2</sub> electrolyzer<sup>29</sup>**

$$\text{Mols of CO}_2 \text{ per second} = \left( \frac{10 \text{ ml CO}_2}{1 \text{ min}} \right) \left( \frac{1 \text{ min}}{60s} \right) \left( \frac{22,400 \text{ ml CO}_2}{1 \text{ mol CO}_2} \right) = \frac{7.4 * 10^{-6} \text{ mol CO}_2}{1s}$$

$$\text{Mols of ethylene per second} = \left( \frac{.255 \text{ C}}{1s} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol C}_2\text{H}_4}{12 \text{ mol e}^-} \right) = \frac{2.2 * 10^{-7} \text{ mol C}_2\text{H}_4}{1s}$$

$$\text{Conversion Percentage} = \frac{2.2 * 10^{-7} \text{ mol C}_2\text{H}_4}{1s} * \frac{1s}{7.4 * 10^{-6} \text{ mol CO}_2} = 2.9\%$$

**H: Verma, S., et al CO<sub>2</sub> electrolyzer<sup>30</sup>**

$$\text{Mols of CO}_2 \text{ per second} = \left( \frac{10 \text{ ml CO}_2}{1 \text{ min}} \right) \left( \frac{1 \text{ min}}{60s} \right) \left( \frac{22,400 \text{ ml CO}_2}{1 \text{ mol CO}_2} \right) = \frac{1.3 * 10^{-5} \text{ mol CO}_2}{1s}$$

$$\text{Mols of CO per second} = \left( \frac{.255 \text{ C}}{1s} \right) \left( \frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left( \frac{1 \text{ mol CO}}{2 \text{ mol e}^-} \right) = \frac{8.3 * 10^{-7} \text{ mol CO}}{1s}$$

$$\text{Conversion Percentage} = \frac{2.2 * 10^{-7} \text{ mol CO}}{1s} * \frac{1s}{7.4 * 10^{-6} \text{ mol CO}_2} = 6.6\%$$

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